

## PATENT ABSTRACTS OF JAPAN

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## (54) MOISTURE-CURABLE COMPOSITION AND POLY (DIALKYLSTANOXANE) DISILICATE COMPOUND

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide moisture-curable compositions which quickly cure and, excel in adhesion and water-resistant adhesion.

SOLUTION: The moisture-curable compositions comprise, as the major components, (A) 100 pts.wt. silyl group-containing organic polymer having at least one silicon atom bonded to a hydrolyzable group at the molecular terminal or in the side chain in the molecule and (B) 0.1-10 pts.wt. curing catalyst which is composed of a reaction product of a poly(dialkylstanoxane) dicarboxylate represented by formula (1) with a silicate compound represented by the formula:  $R_3nSi(OR_4)_{4-n}$ .



**\*NOTICES\***

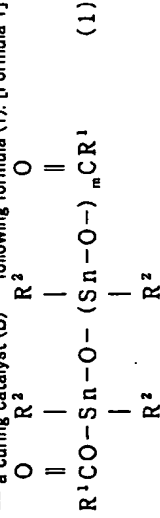
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## CLAIMS

[Claim(s)]

[Claim 1] a molecular terminal — or — a side chain — hydrolytic — a basis — having joined together — a silicon atom — one — a molecule — inside — at least — one — a piece — having — a silyl group — content — organicity — a polymer — (— A —) — 100 — a weight section — a curing catalyst — (— B —) — 0.1 — ten — a weight section — a basis component — carrying out — a constituent — setting — a curing catalyst (B) — following formula (1): [Formula 1]

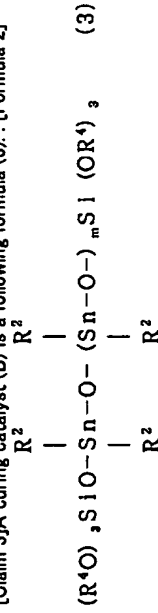


(R<sup>1</sup> and R<sup>2</sup> among a formula) Even if it is a hydrocarbon group with 1-12 carbon atoms independently and two R<sup>1</sup> and R<sup>2</sup> of an individual (2m+2) are the same respectively, it may differ — m — one or more integers — it is — the poly (dialkyl stanoxane) dicarboxylate expressed and following formula (2): R<sub>n</sub><sup>3</sup> Si (OR<sup>4</sup>)<sub>4-n</sub> (2)

(R<sup>3</sup> and R<sup>4</sup> among a formula) Even if it is a hydrocarbon group with 1-4 carbon atoms independently and n R<sup>3</sup> and R<sup>4</sup> of an individual (4-n) are the same respectively, it may differ — n — an integer of 0-3 — it is — a moisture curing nature constituent consisting of a silicate compound expressed and/or a resultant with the hydrolyzate.

[Claim 2] A silicate compound by which a curing catalyst (B) is expressed with poly (dialkyl stanoxane) dicarboxylate expressed with a general formula (1), and a general formula (2), and/or a resultant with the hydrolyzate. The moisture curing nature constituent according to claim 1 being a silicate compound expressed with a general formula (2), and/or a mixture with the hydrolyzate.

[Claim 3] A curing catalyst (B) is a following formula (3) : [Formula 2]

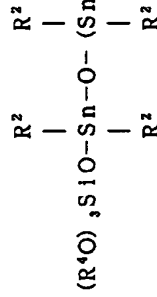


The poly (dialkyl stanoxane) JISHIRIKETO compound expressed with (the inside of a formula,  $R^2$ ,  $R^4$ , and  $m$  are the same as the above). Or the moisture curing nature constituent according to claim 1 being a mixture with this poly (dialkyl stanoxane) JISHIRIKETO compound, tetra alkoxysilane, and/or its hydrolyzate.

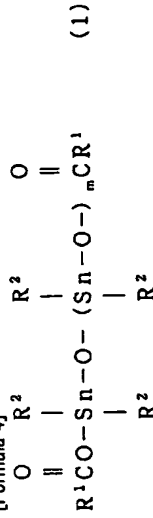
[Claim 4]A following formula (3): [Formula 3]

**[Translation done.]**

(Among a formula,  $R^2$  is a hydrocarbon group with 1-12 carbon atoms, may be the same respectively, or may differ, and  $R^4$  [ of  $R^2$  of an individual ( $2m+2$ ) ] it is a hydrocarbon group with 1-4 carbon atoms, and six  $R^4$  may be the same or may differ —  $m$  — one or more integers — it is — the poly (dialkyl stanoxene) JISHIRIKETO compound expressed.



[Formula 4]



[0007][R<sup>1</sup> and R<sup>2</sup> among a formula] Even if it is a hydrocarbon group with 1-12 carbon atoms independently and two R<sup>1</sup> and R<sup>2</sup> of an individual (2m+2) are the same respectively, it may differ — m — one or more integers — it is — the poly (dialkyl stanoxane) dicarboxylate expressed and following formula (2): R<sup>3</sup><sub>n</sub>Si(OR<sup>4</sup>)<sub>4-n</sub> (2)

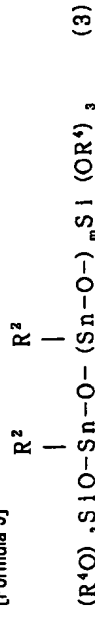
(R<sup>3</sup> and R<sup>4</sup> among a formula) Even if it is a hydrocarbon group with 1-4 carbon atoms independently and n R<sup>3</sup> and R<sup>4</sup> of an individual (4-n) are the same respectively, it may differ — n — an integer of 0-3 — it is — it is related with a moisture curing nature constituent consisting of a silicate compound expressed and/or a resultant with the hydrolyzate.

[0008]A silicate compound by which an invention concerning claim 2 is expressed with poly (dialkyl stanoxane) dicarboxylate to which a curing catalyst (B) is expressed with a general formula (1), and a general formula (2) and/or a resultant with the hydrolyzate, it is related with the moisture curing nature constituent according to claim 1 being a silicate compound expressed with a general formula (2), and/or a mixture with the hydrolyzate.

[0009]In an invention which furthermore relates to claim 3, a curing catalyst (B) is a following formula

(3): [0010]

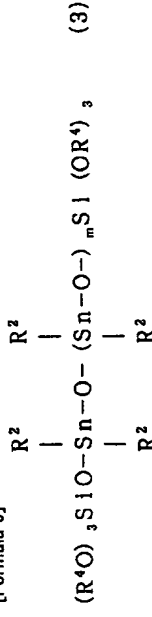
[Formula 5]



[0011]The poly (dialkyl stanoxane) JISHIRIKETO compound expressed with (the inside of a formula, R<sup>2</sup>, R<sup>4</sup>, and m are the same as the above). Or it is related with the moisture curing nature constituent according to claim 1 being a mixture with this poly (dialkyl stanoxane) JISHIRIKETO compound, tetraalkoxysilane, and/or its hydrolyzate.

[0012]An invention which furthermore relates to claim 4 is a following formula (3): [0013]

[Formula 6]



[0014](Among a formula, R<sup>2</sup> is a hydrocarbon group with 1-12 carbon atoms, may be the same respectively, or may differ, and R<sup>4</sup> [ of R<sup>2</sup> of an individual (2m+2) ] it is a hydrocarbon group with 1-4 carbon atoms, and six R<sup>4</sup> may be the same or may differ — m — one or more integers — it is — it is related with the poly (dialkyl stanoxane) JISHIRIKETO compound expressed.

[0015]

[Embodiment of the Invention]The silicon atom which combined with the molecular terminal or the side chain the organic polymer (A) used for this invention with the hydrolytic basis. It is a silyl group content organicity polymer which it has [ (it may be hereafter called the silicon group combined with the hydrolytic basis) and ] in [ at least one ] one molecule, and an alkylene oxide polymer thru/or polyether, an ether ester block copolymer, etc. are mentioned as a main chain of this polymer. The polymer of an

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the moisture curing nature constituent and poly (dialkyl stanoxane) JISHIRIKETO compound which hardened promptly and were excellent in an adhesive property and waterproofing adhesive property.

[0002]

[Description of the Prior Art]As 1 liquid type moisture curing nature rubber, silicone rubber, urethane rubber, polysulfide rubber, etc. are known. Generally 1 liquid type moisture curing nature rubber has quick hardening, and it is excellent that there are no necessities, such as mixed adjustment of liquid, etc. in respect of workability compared with the two-component thing.

[0003]

[Problem(s) to be Solved by the Invention]However, the thing of silicone series rubber has a problem in respect of the possibility of the contamination to the circumference, and the paintwork to the surface, and the thing of urethane system rubber has a problem in respect of storage stability, weatherability, fizz-proof, discoloration, etc. There is a problem in respect of hardenability and the possibility of the contamination to the circumference also about polysulfide system rubber. Although modified silicone system rubber is a polymer which has a hydrolytic silicon functional group which uses polyether as a main chain, and for which a bridge can be constructed and it is stability under seal in the coexistence state of a curing catalyst for a long period of time, When it exposes to humidity, it is 1 liquid setup-of-tooling product which hardens quickly and changes to a rubber-like substance (JP,62-35421,B, JP,61-141761,A, JP,1-58219,A). This polymer has storage stability, weatherability, fizz-proof, and good color fastness compared with a polyurethane system, compared with a polysulfide system, it excels in hardenability, there is little stain resistance to the circumference, and there is no toxicity. There is little stain resistance to the circumference compared with the usual silicone series rubber, and the paintwork to the surface is good. Although a titanate compound, a tin carboxylate compound, amine, etc. are known as a curing catalyst of the polymer which has this hydrolytic silicon group, in these catalysts, an adhesive property, especially waterproofing adhesive property are remarkably inferior, and need to use a primer etc. By JP,59-38989,B, JP,1-58219,B, JP,2-22105,B, JP,58-57460,A, JP,63-18975,B, etc. As a curing catalyst of the polymer which it has, a hydrolytic silicon group use of the resultant of dialkyl tin oxide or carboxylate, and alkoxysilane, In JP,7-11155,A, using a dibutyl tin screw (TORIETOKISHI silicate) as a curing catalyst is proposed. Although the cure rate became quick by use of these ORGANO tin silicate compounds compared with the time of using ORGANO tin carboxylate, development of the catalyst with a cure rate that it is not enough and still quicker was desired.

[0004]

[Means for Solving the Problem]Then, this invention persons inquire wholeheartedly so that they may get a moisture curing nature constituent which hardened promptly and was excellent in an adhesive property and waterproofing adhesive property, and they came to complete this invention.

[0005]Namely, — a claim — one — starting — an invention — a molecular terminal — or — a side chain — hydrolytic — a basis — having joined together — a silicon atom — one — a molecule — inside — at least — one — a piece — having — a silyl group — content — organicity — a polymer — (— A —) — 100 — a weight section — a curing catalyst — (— B —) — 0.1 — ten — a weight section — a basis component — carrying out — a constituent — setting — a curing catalyst — (— B —). Following formula (1): [0006]

ethylene nature unsaturated compound and diene series is mentioned.

[0016]As said alkylene oxide polymer thru/ or polyether,  $(\text{CH}_2\text{CH}_2\text{O})_p$  What has repeating units, such as p

[0017] As a polymer of an ethylene nature unsaturated compound and diene series, Homopolymers, such as ethylene, propylene, acrylic ester, methacrylic acid ester, vinyl acetate, acrylonitrile, styrene, isobutylene, butadiene, isoprene, and chloroprene, or two or more sorts of these copolymers are mentioned. More specifically Polybutadiene, a styrene butadiene copolymer, An acrylonitrile butadiene copolymer, an ethylene-butadiene copolymer, Ethylene propylene rubber, an ethylene-vinylacetate copolymer, an ethylene-acrylic ester copolymer, Polyisoprene, a styrene isoprene copolymer, an isobutylene-isoprene copolymer, Polychloroprene, a styrene chloroprene copolymer, an acrylonitrile chloroprene copolymer, polyisobutylene, polyacrylic ester, polymethacrylic acid ester, etc. are mentioned.

[0018]The silicon group combined with the hydrolytic basis is a basis which causes a condensation reaction by using a catalyst etc. if needed under existence of humidity and a cross linking agent. Specifically, a halogenation silyl group, alkoxy silyl groups, an alkanyl oxyethyl group, an acyloxy silyl group, an amino silyl group, an amino oxyethyl group, an oxime silyl group, and an amide silyl group are mentioned. Here, the number of these hydrolytic bases combined with the silicon atom in the silicon group combined with the hydrolytic basis is chosen from the range of 1-3. The number of the hydrolytic bases combined with one silicon atom may be one, and that of them may be [ two or more ]. Furthermore, the hydrolytic basis and the non-hydrolytic basis may combine with one silicon atom. As a silicon group combined with the hydrolytic basis, handling is an easy point, and especially alkoxy silyl groups (mono- alkoxy silyl groups, a dialkoxy silyl group, and the Tort alkoxy silyl groups are included) is preferred. The silicon group combined with the hydrolytic basis may exist in the end of a polymer molecule, or may exist in the side chain. Even if the silicon group combined with the hydrolytic basis has few polymers per molecule, it is preferred that it averages per molecule from a point of a cure rate and hardened material nature, and there are 1.5 or more pieces with one piece although it is good. A method publicly known as a method of combining with said main chain polymer the silicon group combined with the hydrolytic basis is employable.

[0019] Although the molecular weight of the organic polymer (A) used by this invention does not have restrictions in particular, the thing of the amount of polymers is hyperviscosity, and since it becomes difficult [ a use top ] when it is considered as a hardenability constituent, 30000 or less are too desirable [ a thing ] as a number average molecular weight. Although such an organic polymer can be manufactured by a publicly known method, commercial items, such as KANEKA MS polymer by Kaneka Corp., may be used for it, for example.

[0020] One sort of the silicate compound expressed with the dialkyl tin oxydi carboxylate expressed with a general formula (1) and a general formula (2) as a curing catalyst (B) used for this invention and/or a resultant with the hydrolyzate or two sorts or more are used preferably.

[0021] In said general formula (1), as a hydrocarbon group with 1–12 carbon atoms expressed with  $R^1$  and  $R^2$ , straight chain shape, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *s*-butyl, *t*-butyl, pentyl, hexyl, heptyl, octyl, 2-ethylhexyl, decyl, and lauryl, or a branched chain-like alkyl group, un-replacing, or a substituted phenyl group is mentioned. Two  $R^1$  may be the same and may differ.  $R^2$  of an individual may be the same and may differ ( $2m+2$ ). Although  $m$  should just be one or more integers, it is an integer of 1–3 preferably.

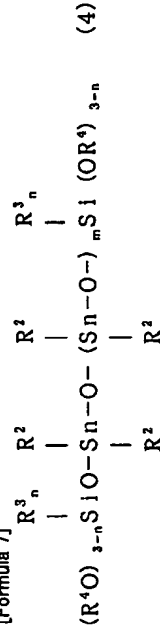
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1,3-bis(lauroyl oxy)distanoxane, 1,1,3,3,5,5-hexamethyl 1,5-bis(acetoxy)tris TANOKISAN, 1,1,3,3,5,5-hexamethyl 1,5-bis(butyryloxy)tris TANOKISAN, 1,1,3,3,5,5-hexamethyl 1,5-bis(octanoyloxy)tris TANOKISAN, 1,1,3,3,5,5-hexamethyl 1,5-bis(hexanoyloxy)tris TANOKISAN, 1,1,3,3,5,5-hexamethyl 1,5-bis(2-ethylhexanoyloxy)tris TANOKISAN, 1,1,3,3,5,5-hexamethyl 1,5-bis(lauroyl oxy)tris TANOKISAN, 1,1,3,3,5,5-hexabutyryl-1,5-bis(acetoxy)tris TANOKISAN, 1,1,3,3,5,5-hexabutyryl-1,5-bis(butyryloxy)tris TANOKISAN, 1,1,3,3,5,5-hexabutyryl-1,5-bis(octanoyloxy)tris TANOKISAN, 1,1,3,3,5,5-hexabutyryl-1,5-bis(hexanoyloxy)tris TANOKISAN, 1,1,3,3,5,5-hexabutyryl-1,5-bis(2-ethylhexanoyloxy)tris TANOKISAN, 1,1,3,3,5,5-hexabutyryl-1,5-bis(lauroyl oxy)tris TANOKISAN, 1,1,3,3,5,5-hexa lauryl 1,5-bis(acetoxy)tris TANOKISAN, 1,1,3,3,5,5-hexa lauryl 1,5-bis(butyryloxy)tris TANOKISAN, 1,1,3,3,5,5-hexa lauryl 1,5-bis(octanoyloxy)tris TANOKISAN, 1,1,3,3,5,5-hexa lauryl 1,5-bis(hexanoyloxy)tris TANOKISAN, 1,1,3,3,5,5-hexa lauryl 1,5-bis(2-ethylhexanoyloxy)tris TANOKISAN, 1,1,3,3,5,5-hexa lauryl 1,5-bis(lauroyl oxy)tris TANOKISAN, Hexa- RUKIRUTORI stanoxane dicarboxylates, such as 1,1,3,3,5,5-hexa lauryl 1,5-bis(lauroyl oxy)tris TANOKISAN, etc. are mentioned. Four or less carboxylate with a number of carbon atoms is more preferred from the ease of removal of the carboxylate which tetrabutyl diacyl oxydi stanoxane and tetra OKUCHIRUJI acyloxy distannoxane were preferred, and tetrabutyl diacyl oxydi stanoxane and tetra OKUCHIRUJI acyloxy distannoxane or 1,1,3,3-tetraoctyl-1,3-bis(acetoxy)distannoxane still more preferably distannoxane or 1,1,3,3-tetraoctyl-1,3-bis(acetoxy)distannoxane.

butyl, and t-butyl, etc. are mentioned as a hydrocarbon group with 1-4 carbon atoms expressed with  $R^3$  and  $R^4$ , n  $R^3$  may be the same and may differ.  $R^4$  of an individual may be the same or may differ (4-n). [0023] In a general formula (2), alkyl groups, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, s-  
[0024] As a silicate compound made to react to the poly (dialkyl stannoxane) dicarboxylate expressed with said general formula (1), the silicate compound expressed with a general formula (2) and/or its hydrolyzate can be used. Specifically A tetramethoxy silane, a tetraethoxysilane, tetra propoxysilane, Tetra alkoxy silane or its hydrolyzates, such as tetra isopropoxysilane and tetra butoxysilane, TORIETOKISHI methylsilane, a TORIETOKISHI ethylsilane, a TORIETOKI Cipro pill silane, doria, such as a Tori ethoxy-SOPUROPURU silane and a TORIETOKISHI butylsilane, — a RUKOKISHI monoalkyl silane or its hydrolyzate. Diethoxy dimethylsilane, diethoxy diethylsilane, a diethoxydipropylsilane, A dialkoxy dialkyl silane or its hydrolyzates, such as a diethoxydiisopropylsilane and a diethoxydiethylsilane, Monoalkoxy trialkyl silanes, such as ethoxy trimethylsilane, an ethoxy triethylsilane, an ethoxy TORIPURO pill silane, an ethoxy triisopropyl silane, and an ethoxy tributylsilane, or the hydrolyzate of those is mentioned. Tetra alkoxy silane or its hydrolyzate is [ among these ] preferred. It is a tetraethoxysilane still more preferably.

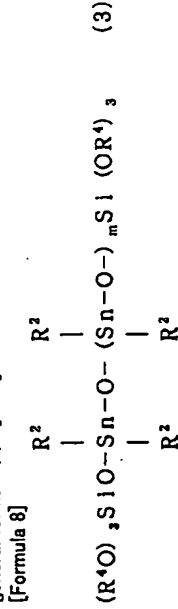
[0025]The poly (dialkyl stanoxane) JISHIRIKETO compound which are poly (dialkyl stanoxane) dicarboxylate, a silicate compound, and/or a resultant with the hydrolyzate. The silicate compound shown by the poly (dialkyl stanoxane) dicarboxylate shown by a general formula (1) and a general formula (2) and/or its hydrolyzate are made to react at 100-130 °C for about 1 to 3 hours, and it is obtained by removing the carboxylate to generate under decompression. As for a reaction ratio, it is preferred to make 1 Eq or more of alkoxy groups react, and to vanish a carboxyl group thoroughly to 1 Eq of carboxyl groups. If the carboxyl group remains, catalytic activity will fall. Although said reaction can be performed under existence of a solvent or absence, it is preferred to usually carry out under the absence of a solvent.

[0026] With a preparation rate with poly (dialkyl stanoxane) dicarboxylate, a silicate compound, and/or its hydrolyzate, etc., although the resultant acquired differs in the structure of a resultant. Following general formula (4) obtained by making 2-6 mol or more react preferably in the silicate compound shown by a general formula (2) to 1 mol of poly (dialkyl stanoxane) dicarboxylate a desirable resultant is indicated to be by a general formula (1): [0027]



$R^2$ ,  $R^3$ ,  $R^4$ , m, and n are the same as the above).

[0028]As opposed to 1 mol of poly (dialkyl stanoxane) dicarboxylate a more desirable resultant is indicated to be by a general formula (1). Following general formula (3) obtained by making 2-6 mol react preferably 2 mol or more in a tetraalkyl silicate compound among the silicate compounds shown by a general formula (2): [0030]



[0031]It is a poly (dialkyl stanoxane) JISHIRIKETO compound expressed with (the inside of a formula,  $R^2$ ,  $R^4$ , and m are the same as the above). The poly (dialkyl stanoxane) JISHIRIKETO compound expressed with a general formula (3) is a new molecular entity.

[0032]Although a resultant of this invention has dramatically high catalytic activity compared with the conventional dialkyl tin compound, it is preferred to mix and use a silicate compound expressed with a general formula (2) and/or its hydrolyzate from the stability of a catalyst and an ease of handling, and the mixture ratio. When making both total quantity into 100 weight sections, it is desirable although it is a silicate compound and/or its one to hydrolyzate 99 weight section to 99 to resultant 1 weight section. They are a silicate compound and/or its ten to hydrolyzate 50 weight section to 90 to resultant 50 weight section still more preferably. After compounding a resultant, even if these mixtures mix a silicate compound and/or its hydrolyzate, they are obtained, or they can be obtained also by the reaction of a silicate compound of an overlarge, and/or its hydrolyzate as dialkyl tin oxydi carboxylate.

[0033]In a moisture curing nature constituent of this invention, content of a curing catalyst (B) has 0.1 - 10 preferred weight section to silyl group content organicity polymer (A) 100 weight section. When said less than range of hardening performance is [ quantity of a curing catalyst (B) ] insufficient and it exceeds said range on the other hand, physical properties, such as recovery of a hardened material after hardening and weatherability, may worsen.

[0034]In order to promote hardening in a moisture curing nature constituent of this invention and to improve adhesion to a substrate, Can use publicly known various amino group substitution alkoxy silane compounds or a condensate of those, and specifically, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, N-(trimethoxysilylpropyl) ethylenediamine, delta-aminobutyl (methyl) diethoxysilane, N,N'-bis(trimethoxysilylpropyl)ethylenediamine, these partial hydrolyseates, etc. are mentioned.

[0035]Additive agents usually added by hardenable constituent, such as a bulking agent, colorant, a plasticizer, a hardening accelerator, a concrete retarder, a dripping inhibitor, an antiaging agent, and a solvent, may be further added to a moisture curing nature constituent of this invention. As a bulking agent, specifically For example, calcium carbonate, kaolin, talc, Fumed silica, sedimentation nature silica, a silicic acid anhydride, hydrous silicic acids, clay, Calcination clay, glass, bentonite, organic bentonite, a mill balloon, glass fiber, asbestos, grinding quartz, diatomite, aluminum silicate, aluminum hydroxide, a zinc oxide, magnesium oxide, a titanium dioxide, etc. are mentioned. Specifically as colorant, iron oxide, carbon black, copper phthalocyanine blue, Phthalocyanine Green, etc. are mentioned. As a plasticizer, specifically Dibutyl phthalate, dioctyl phthalate, Phthalic ester, such as butylbenzyl phthalate, dioctyl adipate, Succinic acid dioctyl, succinic acid diisodecyl, diisodecyl sebacate, Glycol ester, such as aliphatic-carboxylic-acid ester species, such as butyl oleate, and pentaerythritol ester. Epoxy system plasticizers, such as phosphoric ester, such as trioctyl phosphate and tricresyl phosphate, epoxidized soybean oil, and epoxy stearic acid benzyl, a chlorinated paraffin, etc. are mentioned. Specifically as a dripping inhibitor, hydrogenation castor oil, a silicic acid anhydride, organic bentonite, colloidal silica, etc. are mentioned. As other additive agents, adhesion grant agents, such as phenol resin and an epoxy resin, an ultraviolet ray absorbent, radical chain inhibitor, a peroxide decomposition agent, various kinds of antiaging agents, etc. are mentioned.

[0036]

[Example]Although an example is given to below and this invention is concretely explained to it, the range of this invention is not limited by this.

[0037]Example of manufacture 1 thermometer, a reflux condenser, and an agitator in the 500-ml 4 Thru mouth flask which it had under a nitrogen air current, 49.8 g (0.2 mol) of dibutyltin oxide, the acetic anhydride 10.4g (0.1 mol). And after teaching 200 g of toluene and making it react at 112 ° for 2 hours, toluene was distilled off under decomposition and 1,1,3,3-tetrabutyl 1,3-bis(acetoxy)distannoxane was obtained (this compound was obtained quantitatively). Subsequently, taught 41.7 g (0.2 mol) of tetraethoxysilanes (ethyl ortho silicate), it was made to react at 120 ° for 3 hours, the ethyl acetate generated under decomposition was distilled off, and tin compound A 79.8g (yield it is the same as that of the value based on 95% and tin oxide and the following) of the light yellow fluid was obtained. This compound is absorption (1638 cm) of tin carbonyl at FT-IR. [  $^{-1}$  and ] From the result of disappearance of 1559- $cm^{-1}$ , and absorption (477- $cm^{-1}$ ) of Sn-O-Sn and the next ultimate analysis, it checked that they were 1, 1, 3, and 3-tetrabutyl 1 and 3-bis(TORIEKISHI siloxy)distannoxane.

C(%) H(%) O(%) Si(%)Sn(%)  
Measured value 40.1 7.7 17.0 6.9 28.3 theoretical values 40.0 7.9 17.1 6.7 28.3[0038]In the same 4 mouth flask as the example 1 of example of manufacture 2 manufacture, 74.7 g (0.3 mol) of dibutyltin oxide, The acetic anhydride 10.2g (0.1 mol) and 200 g of toluene are taught. React and process like the example 1 of manufacture, and 1, 1, 3, 3, 5, and 5-hexabutyl- 1 and 5-bis(acetoxy)tris TANOKISAN are obtained. Subsequently, 41.7 g (0.2 mol) of ethyl ortho silicate was prepared, it reacted and processed like the example 1 of manufacture, and the tin compound B102.4g (94% of yield) of the light yellow fluid was obtained. This compound is absorption (1638 cm) of tin carbonyl at FT-IR. [  $^{-1}$  and ] From the result of disappearance of 1559- $cm^{-1}$ , and absorption (477- $cm^{-1}$ ) of Sn-O-Sn and the next ultimate analysis, it checked that they were 1, 1, 3, 3, 5, and 5-hexabutyl- 1 and 5-bis(TORIEKISHI siloxy)tris TANOKISAN.

C(%) H(%) O(%) Si(%)Sn(%)  
Measured value 39.9 7.7 14.6 5.1 32.9 theoretical values 39.7 7.8 14.7 5.1 32.7[0039]In the same 4 mouth flask as the example 1 of example of manufacture 3 manufacture, 72.2 g (0.2 mol) of dioctyl tin oxide, The acetic anhydride 10.2g (0.1 mol) and 200 g of toluene are taught. It reacted and processed like the example 1 of manufacture, and 1, 1, 3, and 3-tetraoctyl- 1 and 3-bis(acetoxy)distannoxane were obtained, subsequently prepared 41.7 g (0.2 mol) of ethyl ortho silicate. It was made to react at 120 ° for 3 hours, and tin compound C 101.2g (97% of yield) of the light yellow fluid was obtained. This compound is absorption (1638 cm) of tin carbonyl at FT-IR. [  $^{-1}$  and ] From the result of disappearance of 1559- $cm^{-1}$ , absorption (477- $cm^{-1}$ ) of Sn-O-Sn, and the next ultimate analysis, it checked that they were 1, 1, 3, and 3-tetraoctyl- 1 and 3-bis(TORIEKISHI siloxy)distannoxane.

C(%) H(%) O(%) Si(%) Sn(%)  
Measured value 49.6 9.4 13.6 5.2 22.2 theoretical values 49.6 9.3 13.5 5.3 22.3[0040]In the same 4 mouth flask as the example 1 of example of manufacture 4 manufacture, 108.3 g (0.3 mol) of dioctyl tin oxide, The acetic anhydride 10.2g (0.1 mol) and 200 g of toluene are taught. React and process like the example 1 of manufacture, and 1, 1, 3, 3, 5, and 5-hexaocetyl- 1 and 5-bis(acetoxy)tris TANOKISAN are obtained. Subsequently, 41.7 g (0.2 mol) of ethyl ortho silicate was prepared, it reacted and processed like the example 1 of manufacture, and tin compound D 135.5g (95% of yield) of the light yellow fluid was obtained. This compound is absorption (1638 cm) of tin carbonyl at FT-IR. [  $^{-1}$  and ] From the result of disappearance of 1559- $cm^{-1}$ , and absorption (477- $cm^{-1}$ ) of Sn-O-Sn and the next ultimate analysis, it checked that they were 1, 1, 3, 3, 5, and 5-hexaocetyl- 1 and 5-bis(TORIEKISHI siloxy)tris TANOKISAN.

C(%) H(%) O(%) Si(%)Sn(%)  
Measured value 50.4 9.5 11.2 3.8 25.1 theoretical values 50.5 9.4 11.2 3.9 25.0[0041]In the same 4 mouth flask as the example 1 of example of manufacture 5 manufacture, 33.0 g (0.2 mol) of dimethyl tin oxide, The acetic anhydride 10.2g (0.1 mol) and 200 g of toluene are taught. It reacted and processed like the example 1 of manufacture, and 1, 1, 3, and 3-tetramethyl 1 and 3-bis(acetoxy)distannoxane were obtained, subsequently 41.7 g (0.2 mol) of ethyl ortho silicate was prepared, it reacted and processed like the example 1 of manufacture, and tin compound E 63.8g (95% of yield) of the light yellow fluid was obtained. This compound is absorption (1638 cm) of tin carbonyl at FT-IR. [  $^{-1}$  and ] From the result of disappearance of 1559- $cm^{-1}$ , and absorption (477- $cm^{-1}$ ) of Sn-O-Sn and the next ultimate analysis, it checked that they were 1, 1, 3, and 3-tetramethyl 1 and 3-bis(TORIEKISHI siloxy)distannoxane.

C(%) H(%) O(%) Si(%)Sn(%)



